Short communication

The fabrication of silver ion implantation-modified electrode and its application in electrocatalytic oxidation of formaldehyde

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HIGHLIGHTS

- A novel process for the fabrication of a silver-nanoparticle-modified electrode using ion implantation.
- The zero-valent state of AgNPs exhibit well catalytic performance and stability towards the electro-oxidation of formaldehyde.
- AgNPs/ITO electrode may be a promising anode electrode material for the direct formaldehyde fuel cells (DFFCs).

GRAPHICAL ABSTRACT
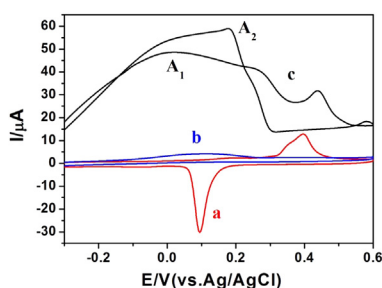
ARTICLE INFO

ABSTRACT

In this work, we present a novel process for the fabrication of a silver-nanoparticle-modified electrode using silver ion implantation. This method is facile, low-cost and environmental friendly without the use of any linking chemicals. The modified electrode was verified by scanning electron microscope (SEM), atomic force microscope (AFM), X-ray photoelectron spectroscopy (XPS), electrochemical impedance spectra (EIS) and cyclic voltammetry (CV). The AgNPs formed on the electrode are in the zero-valent metallic state with a size distribution in the range of 3–6 nm. The modified electrode shows prominent electrocatalytic activity towards the oxidation of formaldehyde with long-term stability and could be useful in fuel cells.

1. Introduction

The electrochemical oxidation of small organic molecules such as methanol, ethanol, formic acid and formaldehyde have been investigated intensively for the development of direct fuel cells due to the relative ease of storage and handling as well as high energy density [1–6]. Several reports have been published on the electrochemical oxidation of methanol and many of them were carried out on noble metal electrodes [7–11]. In recent years, there has been increasing interest in the electrochemical oxidation of formaldehyde [12–15].

Noble metals such as Pt and Pd are initially good catalysts for the electro-oxidation of small organic molecules. Numerous reports have been published on the oxidation of formaldehyde and most of them are carried out on Pt or Pd catalyst [6,16,17]. However, the high cost of noble metals inhibits their application in fuel cells. Therefore, the effort to finding out an abundant, inexpensive and efficient electrocatalytic material as the substitute for noble metal catalysts is of great significance. Ag is much cheaper than Pt and Pd. It has the highest electrical conductivity among the metals and silver nanoparticles (AgNPs) have been explored traditionally to be

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employed as catalysts in various reactions [18–20]. In recent years, there are myriads of methods to prepare AgNPs, such as chemical reduction [21], electrochemical deposition [22], drop casting [23] and metal-vapor synthesis [24]. Nevertheless, it is still expected that the less use of stabilizers and binding reagents would improve the performance of the modified electrode significantly in the consideration of the negative effects brought by these chemicals.

Ion implantation is a kind of material surface modification technique, which provides practical and excellent electrode materials with long-term stability. By this method, we can modify the metallic nanoparticles on the substrate and control their size just by the implantation condition. In addition, the process is facile, low-cost and eco-friendly without the use of any other chemicals [25–30]. In our previous reports, we have prepared several metal-nanoparticle-modified electrodes successfully by ion implantation [7,31,32]. These electrodes exhibited very low background current and excellent electrochemical stability, even after ultrasonic treatment, indicating the high stability of the nanoparticles on the surface. Indium tin oxide (ITO) was chosen as the electrode substrate due to its wide electrochemical working window and stable electrochemical properties [33–36]. In addition, it can be available at a very low cost from industrial mass production.

In this paper, our group describes a new method to prepare AgNPs modified ITO electrode (AgNPs/ITO) by silver ion implantation. The prepared AgNPs on the ITO electrode surface are free from any chemical reagents surrounding or binding to them. The AgNPs/ITO electrodes were used for the electrocatalytic oxidation of formaldehyde and exhibited remarkable catalytic activity with good stability.

2. Experimental

2.1. Reagents

ITO glass was purchased from Beijing Tsinghua Engineering Research Center of Liquid Crystal Technology. All chemicals were of analytical grade and used as purchased without further purification. All measurements were performed at room temperature. All solutions were prepared with triple distilled water.

2.2. Preparation of the AgNPs/ITO electrode

Ion implantation was carried out using a Beijing Normal University (BNU) metal vapor vacuum arc (MEVVA) implanter. Silver ions with 10 KeV at the fluences of 1.0×10^{17} ions cm^{-2} were implanted onto the pretreated ITO surface, forming the AgNPs/ITO electrode. According to our experience, the fluence and energy we used could implant the maximum amount of AgNPs on the substrate and retain the electrical conductivity of the electrode. The electrode was washed with distilled water and ethanol for several times before used.

2.3. Apparatus

The structure and morphology of the electrode were characterized by scanning electron microscope (SEM) (Hitachi X650, Japan). Tapping mode atomic force microscope (AFM) images were recorded by using a Nanoscope Instrument (Vecco). X-ray photoelectron spectroscopy (XPS) measurement was performed on an AXIS Ultra spectrometer (Shimadzu, Japan). All electrochemical measurements were carried out on a CHI660D electrochemical workstation (CH Instrument Inc, USA). A conventional three-electrode system was employed with a bare or modified ITO electrode ($A = 75$ mm^2) as the working electrode, an Ag/AgCl electrode

(saturated KCl) as the reference electrode, and a platinum wire electrode as the auxiliary electrode.

3. Results and discussion

3.1. Characterization of AgNPs/ITO electrode

3.1.1. SEM images of AgNPs/ITO electrode

Fig. 1 (A) shows the structure of the bare ITO electrode surface. As seen in this image, there are some spherical-shaped grains on the bare ITO electrode surface. After ion implantation, we can observe a distinct change in the surface as a result of the formation of AgNPs (Fig. 1(B)). It shows clearly that the spherical-shaped grains disappeared and the highly dispersed AgNPs with diameters between 3 and 6 nm emerged on the modified electrode.

3.1.2. AFM studies of AgNPs/ITO electrode

Fig. 2 illustrates the three-dimensional view of the tapping mode image of the bare ITO (A) and the AgNPs/ITO (B). From AFM measurement, it is given that the surface roughness (Rrms) of the bare ITO and the AgNPs/ITO is 1.76 and 1.36, respectively. As can be seen from the figure and Rrms data, the bare ITO surface is so coarse, but the AgNPs/ITO electrode surface becomes smoother after silver ion implantation. The results confirm the morphological change of the ITO after ion-implantation, which might be attributed to the creation of a new interface after bombardment by heavy ions [28,37].
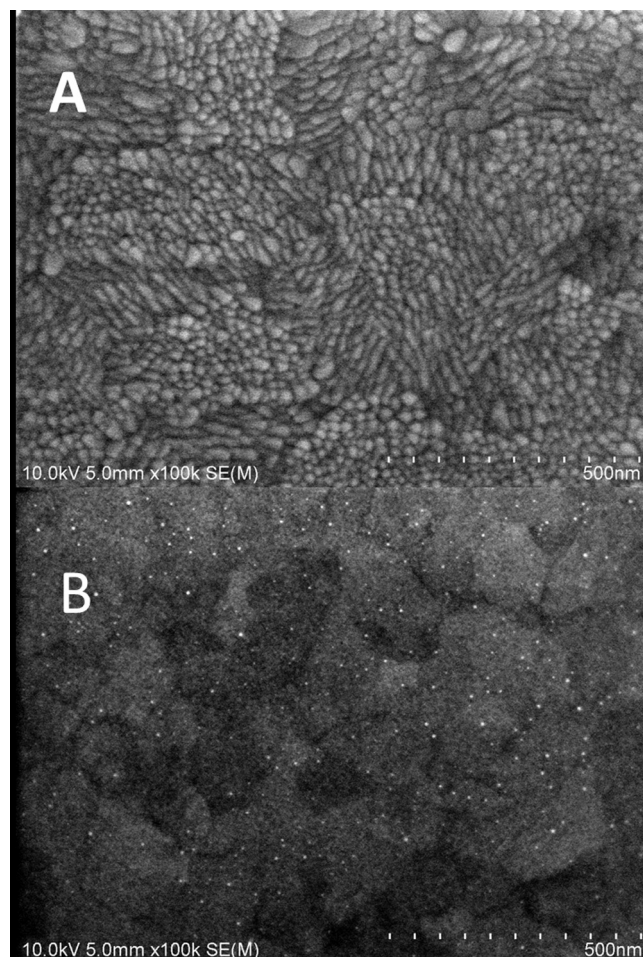

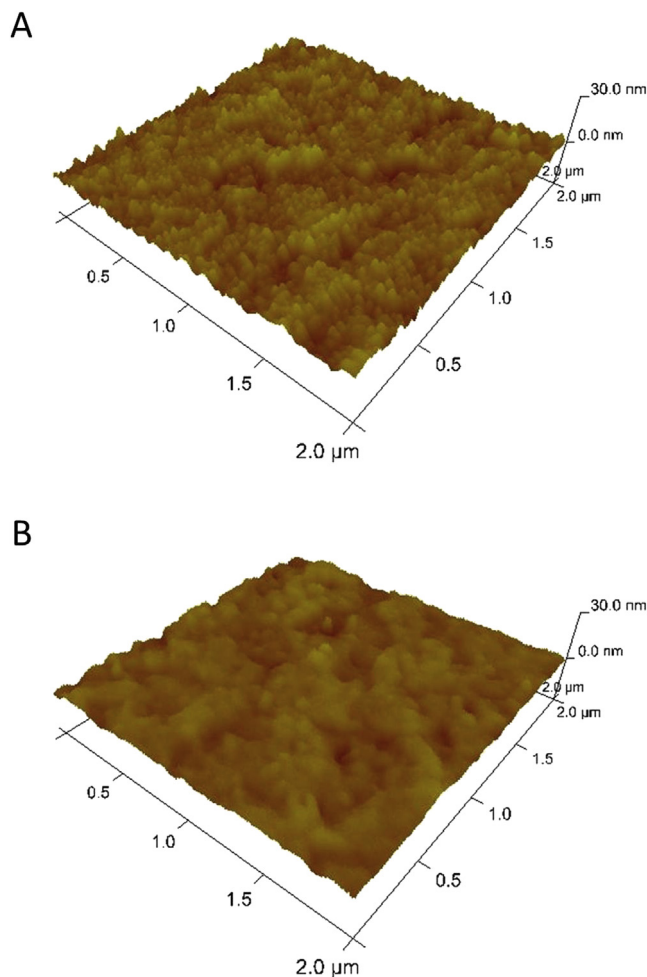**Fig. 1.** SEM images of the bare ITO (A) and the AgNPs/ITO (B).

A

B

Fig. 2. AFM images of the bare ITO electrode (A) and the AgNPs/ITO electrode (B).

3.1.3. XPS analysis of AgNPs/ITO electrode

To give further evidence that Ag is implanted on the modified electrode, the XPS experiment was carried out. Fig. 3 shows the XPS survey spectrum of the AgNPs/ITO electrode. Two strong satellite peaks at 368.4 eV and 374.4 eV correspond to Ag ($3d_{5/2}$) and Ag ($3d_{3/2}$) were observed. It can be concluded that the implanted Ag is int the zero valent metallic state by comparing the binding
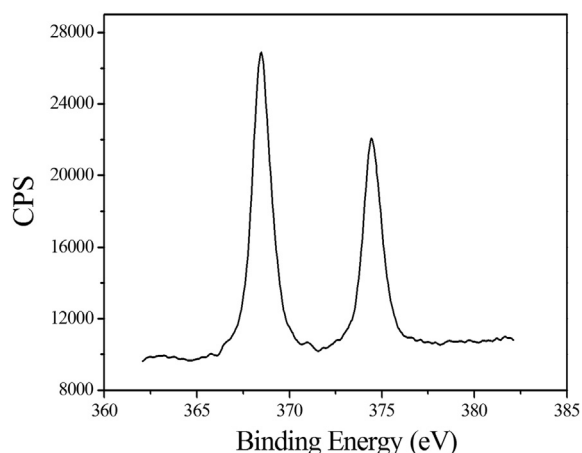

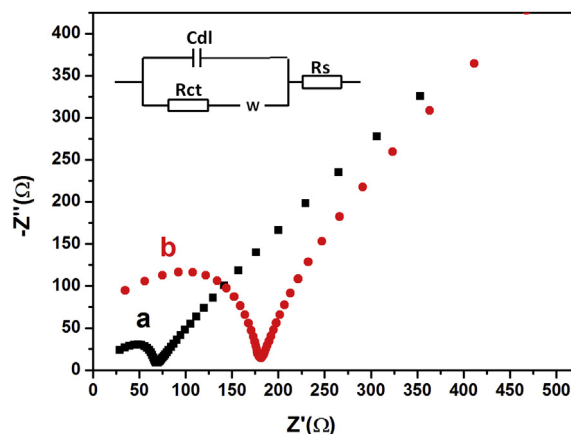**Fig. 3.** XPS spectrum of the AgNPs/ITO electrode.

Fig. 4. EIS of the bare ITO electrode (a) and the AgNPs/ITO electrode (b) in the presence of 1.0 mM $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ (1:1) and 0.1 M KCl solution, respectively. EIS conditions: potential, 0.2 V; alternative voltage, 5 mV; frequency range, $10–10^6$ Hz.

energies. This result indicates that we have successfully implanted AgNPs onto the ITO electrode surface.

3.1.4. Electrochemical behaviors of the AgNPs/ITO electrode with EIS

EIS was carried out to characterize the impedance change of the electrode surface in the modification process. In EIS, the semi-circle diameter equals the interface electron-transfer resistance (R_{ct}), which controls the electron-transfer kinetics of the redox probe at the electrode interface. To give more detailed information about the electrical properties of the different electrodes, the Randles circuit (inset of Fig. 4) was chosen to fit the obtained impedance data. Fig. 4 shows the complex−plane impedance spectra (-Z″ vs. Z′, Nyquist plot) of the EIS obtained at the bare ITO (a) electrode and the AgNPs/ITO electrode (b). The Rct on the bare ITO is about 50 Ω. However, the Rct on the AgNPs/ITO electrode increases to about 180 Ω. The diameter of the semicircle for the AgNPs/ITO electrode is larger than that of the bare ITO electrode, revealing that the implantation of silver on the surface of ITO creates a new interface between the probe and the electrode surface.

3.1.5. Electrochemical behaviors of the AgNPs/ITO electrode with CV

CV is a significant method to demonstrate electrochemical properties of the AgNPs/ITO. Fig. 5 shows the CVs of the bare ITO (a) and the AgNPs/ITO (b) in 0.1 M NaOH. We do not find any peaks on
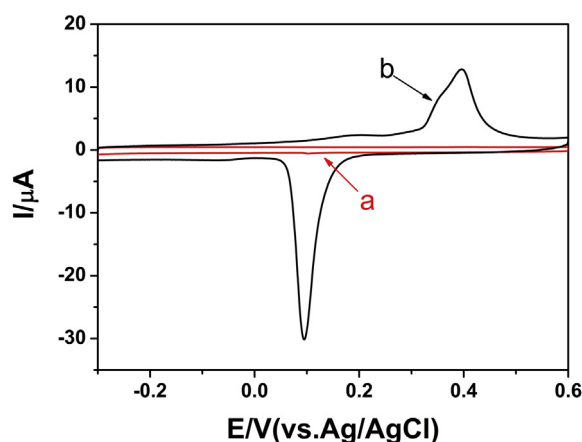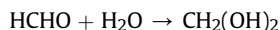

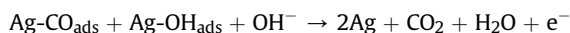**Fig. 5.** CVs of the bare ITO (a) and the AgNPs/ITO (b) in 0.1 M NaOH at a scan rate of 100 mV s^{-1}.
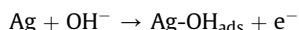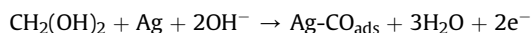
the bare ITO as shown in Fig. 4(a). In contrast, the AgNPs/ITO shows an anodic peak appearing at 0.41 V in the anodic potential sweep, along with a cathodic peak at 0.09 V during the reverse scan. According to the reports [38,39], the anodic peak (0.41 V) is attributed to the oxidation of silver (0) to silve (I).

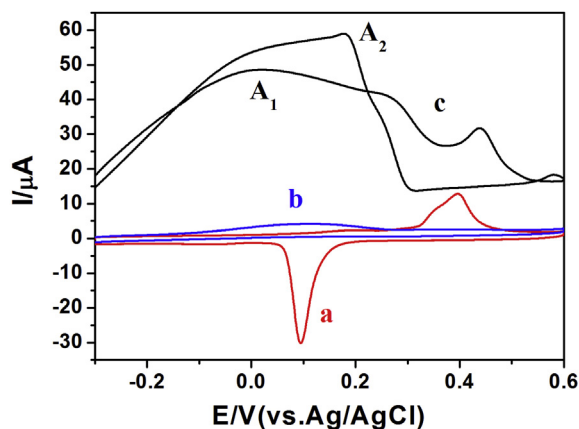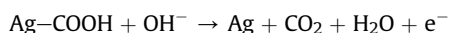## 3.2. The electrocatalytic oxidation of formaldehyde

Fig. 6 shows the CVs of the AgNPs/ITO in the absence of formaldehyde (a), the bare ITO (b) and the AgNPs/ITO (c) in the presence of 0.1 mM formaldehyde in 0.1 M NaOH. The line c shows two irreversible current peaks during the formaldehyde oxidation: a forward scan peak at 0.003 V and a backward peak at 0.177 V. The large oxidation current (peak A_1) represents the pronounced formaldehyde oxidation during the anodic scan. The other large oxidation current (peak A_2) in the reverse scan is attributed to the removal of the incompletely oxidized carbonaceous species formed in the forward scan [40–42]. According to the CV results and previous reports, we elucidated following mechanism for the formaldehyde oxidation [13,43–45]. Formaldehyde is oxidized to CO_2 via a dual path mechanism, which involves a reactive intermediate and adsorbed CO as poisoning species. In one pathway, the direct oxidation of formaldehyde occurs (pathway2). Whereas in the other pathway, formaldehyde is oxidized to CO (pathway 1), which in turns would be removed. At higher potentials, a quick increase in current is observed during the intermediate being oxidized further by silver (I), which aids in transforming the poisonous intermediates to CO_2. The surface poison shown in pathway1 can be removed by reacting with OH_{ads} .

$$HCHO + H_2O \rightarrow CH_2(OH)_2$$

Pathway 1:

$$CH_2(OH)_2 + Ag + 2OH^- \rightarrow Ag\text{-}CO_{ads} + 3H_2O + 2e^-$$

$$Ag + OH^- \rightarrow Ag\text{-}OH_{ads} + e^-$$

$$Ag\text{-}CO_{ads} + Ag\text{-}OH_{ads} + OH^- \rightarrow 2Ag + CO_2 + H_2O + e^-$$

Pathway 2:

$$CH_2(OH)_2 + Ag + 3OH^- \rightarrow Ag\text{-}COOH + 3H_2O + 3e^-$$

$$Ag\text{-}COOH + OH^- \rightarrow Ag + CO_2 + H_2O + e^-$$

Fig. 7. CVs of the AgNPs/ITO in the presence of 0.1 mM formaldehyde in 0.1 M NaOH at various scan rates of 80, 100, 120, 140, 160, 180, and 200 mV s^{-1} (from inner to outer). Inset: peak currents (peak A_1) versus scan rates.

During the above process, the formation and adsorption of intermediates (CO) poisoned the electrode surface. However, the results reflected that the AgNPs/ITO electrode possessed a high resistance to CO during the formaldehyde oxidation, indicating that the AgNPs/ITO electrode had an acceptable electrocatalytic activity towards the electro-oxidation of formaldehyde.

Fig. 7 shows the CVs of the AgNPs/ITO electrode in the presence of 0.1 mM formaldehyde in 0.1 M NaOH at different scan rates. The results demonstrate that the anodic peak current at about 0.003 V (peak A_1) has linear relation with the square root of the scan rate (inset of Fig. 6) and the linear regression equation is ipa (μA) = 2.1059 + 1.1543$V^{1/2}$ (mV s^{-1})$^{1/2}$, with a correlation coefficient of 0.9986, which suggests that the formaldehyde electrooxidation is a diffusion-controlled process.

High catalytic stability represents another attractive feature of the newly constructed metal nanoparticles modified electrode. Fig. 8 shows the chronoamperometric curves of the AgNPs/ITO electrode in the solution of 0.1 M NaOH towards 0.1 mM formaldehyde at a constant potential of 0.22 V versus Ag/AgCl for 1000 s. It is found that the current observed from chronoamperograms is in good agreement with the current observed from the cyclic voltammetry. The current maintains a relatively stable trend after 200 s. This result suggests that the AgNPs/ITO electrode has a good stability for the oxidation of formaldehyde, with the superior CO-
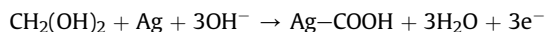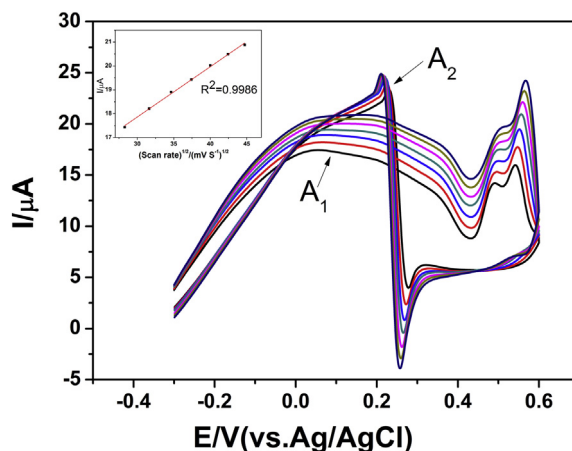
Fig. 6. CVs of the AgNPs/ITO in the absence of formaldehyde (a), the bare ITO (b) and the AgNPs/ITO (c) in the presence of 0.1 mM formaldehyde in 0.1 M NaOH. Scan rate: 100 mV s^{-1}.
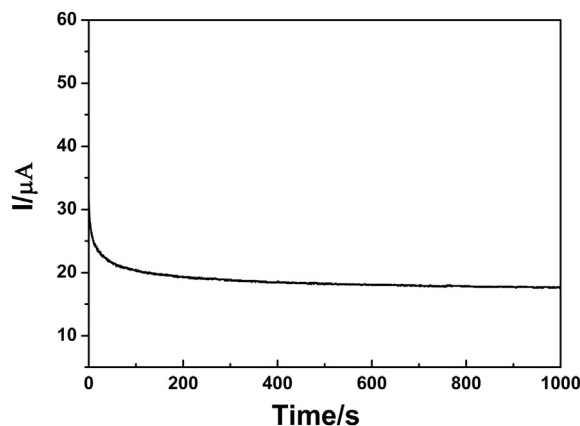
Fig. 8. Chronoamperometric responses of the AgNPs/ITO electrode in 0.1 M NaOH towards 0.1 mM formaldehyde.

tolerance active surface area. The proposed modified electrode was stored in air at ambient conditions and its sensitivity was checked every week. The response was 95% of its initial value after 30 days, which shows the long-term stability of this electrode for the oxidation of formaldehyde. In addition, the electrode surface could be easily cleaned by ultrasonic treatment.

4. Conclusions

In this work, AgNPs have been modified onto ITO electrodes by ion implantation to prepare a novel functional electrode. It has been proved to be a facile, effective and eco-friendly method which would potentially be used to manufacture modified electrodes in industrial large-scale. The proposed electrode exhibited high electrocatalytic activity towards the oxidation of formaldehyde, showing a satisfactory stability and reproducibility when stored in ambient conditions or continues cycling, making it an attractive anode for the fabrication of direct formaldehyde fuel cells (DFFCs).

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